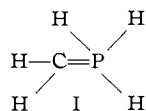


coupling to  $^{31}\text{P}$  than to  $^1\text{H}$  or  $^{13}\text{C}$  due both to the greater anisotropy of the screening around phosphorus<sup>8</sup> and to the relatively small degree of s-character of its bonding orbitals.<sup>9</sup> However, Klose has been able to justify the spectrum of  $(\text{CH}_3\text{CH}_2)_3\text{P}$  semiquantitatively by a valence-bond treatment using only contact interactions.<sup>2</sup> Alternately, the d orbitals and nonbonding electrons of phosphorus may be involved in coupling through structures of the "ylene" type (I).<sup>10</sup> Spin-orbital or magnetic-dipole interactions might give



$J_{\text{PCH}}$  the observed sign; important contributions from I certainly would. It is not possible to decide which factor is most important on the basis of available experimental evidence.

It is unfortunately not possible to assign an absolute sign to  $J_{\text{PH}}$ , although such an assignment would be of considerable interest. Recent calculations for several paramagnetic transition metal ions indicate that the contributions of a spin-polarized 3s orbital to the contact term may be opposite in sign to that of a 1s or 2s orbital<sup>11</sup>; this result suggests that  $J_{\text{PH}}$  may be either positive or negative, depending upon the relative contributions of the 1s, 2s, and 3s electrons to the coupling.

**Acknowledgment.**—We are deeply indebted to Dr. F. C. Caserio, Jr., for the phosphine samples used in this research.

(8) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

(9) The bond angles in methylphosphine suggest that the phosphorus bonding orbitals in this compound have predominantly p-character:  $\angle\text{CPH} = 97^\circ 30'$ ,  $\angle\text{HPH} = 93^\circ 23'$ ; see E. L. Breig and C. C. Liu, *J. Chem. Phys.*, **35**, 2139 (1961).

(10) This structure is analogous to the hyperconjugative structures used to explain long range coupling in hydrocarbons. Although unimportant in determining the total energy of the molecule, such structures may be very important in spin-spin coupling. See R. A. Hoffman and S. Gronowitz, *Arkiv. Kemi.*, **16**, 471 (1960).

(11) V. Heine, *Phys. Rev.*, **107**, 1002 (1957); R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1125, 1134 (1960).

(12) National Science Foundation Undergraduate Research Participant, 1962.

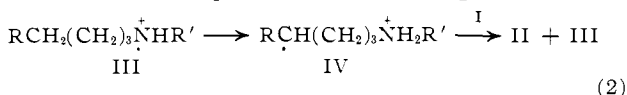
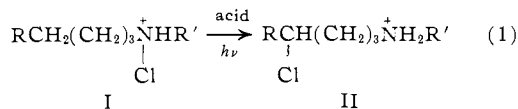
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PASADENA, CALIFORNIA JOHN D. ROBERTS

RECEIVED JULY 1, 1963

### The Chemistry of Ion Radicals. The Free Radical Addition of N-Chlorodialkylamines to Butadiene

Sir:

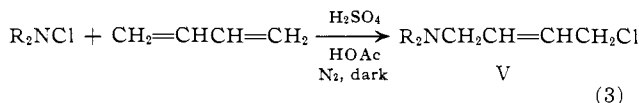
N-Chlorodialkylamines (I) may be rearranged<sup>1</sup> in strongly acidic media under the influence of light, heat, or ferrous ion to the corresponding 4-chloroalkylamines (II) (eq. 1). The sequence  $\text{I} \rightarrow \text{II}$  (the Hofmann-Loef-



- a, R = H, R' = n-C<sub>4</sub>H<sub>9</sub>  
b, R = CH<sub>3</sub>, R' = n-C<sub>8</sub>H<sub>17</sub>  
c, R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>

(1) A review summarizing the various synthetic applications of this reaction is now available: M. E. Wolf, *Chem. Rev.*, **63**, 55 (1963). However, some of our data, to be reported in the near future, appear to contradict certain of the hypotheses presented therein concerning the optimum conditions and acidity dependence of the photolytic reaction.

fler reaction) proceeds *via* the ion radical III and the alkyl radical IV (eq. 2).<sup>2,3</sup> However, we have found that the process  $\text{III} \rightarrow \text{IV}$  does not take place when N-chloroamines are treated with olefins. In particular, butadiene reacted rapidly (in 15 min.) and spontaneously with Ia-c in acidic media, exclusively *via* the aminium radical III, to afford the 1-chloro-4-dialkylamino-*trans*-2-butenes Va-c (eq. 3) in yields up to 60% (Table I, entries 1, 6, and 7). In each case butadiene was bubbled into a 0.5 M solution of the chloroamine in 4 M sulfuric acid-wet acetic acid under nitrogen at 5–10°; dilution of the reaction mixture with water followed by basification afforded the product. In the presence of oxygen, Va was not obtained from Ia, but instead 72% of dibutylamine and 7% of the neutral products of ionic chlorination, 1-acetoxy-4-chloro-2-butene and 1-chloro-2-acetoxy-3-butene, were isolated. This result and the structure of the adduct V indicate the transformation (eq. 3) to be a free radical chain process. Structure proof of the 1,4-chloroamination products V was based on the infrared and n.m.r. spectra of the amines, elemental analysis of their picrates, and conversion of Va with dibutylamine in benzene to 1,4-bis(dibutylamino)-*trans*-2-butene, also obtained independently from 1,4-dibromo-*trans*-2-butene and dibutylamine.



Even the aminium radical IIIc reacted exclusively by addition to butadiene (Table I, entry 7) in preference to intramolecular hydrogen abstraction ( $\text{III} \rightarrow \text{IV}$ ), although the potential carbon radical IVc was benzylic. Therefore, the free radical 1,4-chloroamination of butadiene by N-chlorodialkylamines *via* the ion radical III is a general reaction representing a useful synthetic route to reactive trifunctional compounds of type V. This process resembles other radical 1,4-additions to butadiene,<sup>4</sup> but contrasts with the reported<sup>5</sup> addition of aminium radicals derived from hydroxylamines, followed by coupling, which yielded only 1,8-diamino-octadienes. The presence of the positive charge at the radical center appears to exert no unusual effect upon the course of reaction 3. It is expected, however, that further studies of diene systems now in progress will demonstrate particular effects due to the fully ionic nature of the aminium radical.

Other solvents (Table I, entries 2–5) gave lower yields of the adduct V and increased amounts of the parent dialkylamine. The unprotonated chloroamine (in carbon tetrachloride) failed to undergo any reaction with butadiene, even under strong irradiation (Table I, entry 5). Either the neutral species  $\text{R}_2\text{N}\cdot$  was not formed, or it did not add to the diene. Only trifluoroacetic acid (Table I, entries 3 and 8) is a useful alternative solvent to the usual sulfuric acid-acetic acid (Table I, entries 1, 6 and 7), because it can be easily removed under reduced pressure to give the ether-soluble trifluoroacetate salt of the adduct V. In one example (Table I, entry 8) this salt was directly converted with acetic acid-sodium acetate to the acetoxy derivative, thereby

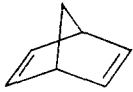
(2) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, **72**, 2118 (1950); S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959).

(3) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

(4) J. K. Kochi, *ibid.*, **84**, 2785 (1962); A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. H. Hudson, Jr., *ibid.*, **84**, 3897 (1962); M. Asscher and D. Vofsi, *Chem. Ind. (London)*, 209 (1961); S. J. Cristol and K. L. Nagpal, *J. Org. Chem.*, **26**, 365 (1961); F. Minisci and R. Galli, *Tetrahedron Letters*, **No. 12**, 533 (1962).

(5) C. J. Alibisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. F. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

TABLE I  
 REACTIONS OF N-CHLORODIALKYLAMINES WITH OLEFINS<sup>a</sup>

Entry	Chloroamine <sup>b</sup>	Olefin <sup>c</sup>	Solvent <sup>d</sup>	Products <sup>e</sup>	Yield, %
1	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NCl	CH <sub>2</sub> =CHCH=CH <sub>2</sub>	A	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> Cl <sup>f</sup> R <sub>2</sub> NH	60 9
2			70% aq. H <sub>2</sub> SO <sub>4</sub>	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> Cl	52
3			B	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> Cl R <sub>2</sub> NH	30 27
4			4 M H <sub>2</sub> SO <sub>4</sub> in nitro- methane	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> Cl R <sub>2</sub> NH	5 34
5			CCl <sub>4</sub> /hν, <sup>g</sup> 2 hr.	no reaction	..
6	( <i>n</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NCl		A	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> Cl <sup>h</sup> R <sub>2</sub> NH	42 22
7	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>4</sub> N(Cl)CH <sub>2</sub>		A	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> <sup>i</sup> R <sub>2</sub> NH	53 13
8	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCl		B	R <sub>2</sub> NCH <sub>2</sub> CH=CHCH <sub>2</sub> OAc <sup>j</sup>	24
9	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NCl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub> <sup>k</sup>	A	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCl R <sub>2</sub> NH	66 84
10	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCl		A	(VI + VII) <sup>k</sup> (VIII + IX) <sup>l</sup>	31 30

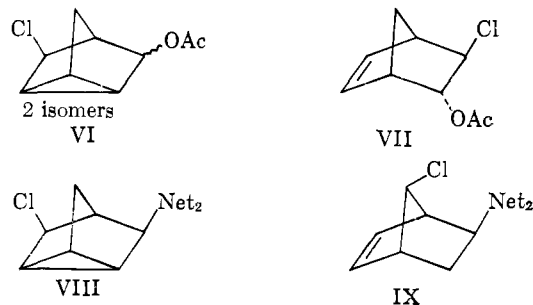
<sup>a</sup> Every reaction (under nitrogen) proceeded spontaneously and rapidly (less than 30 min.) in the dark between -5 and +15°. <sup>b</sup> The chloroamines were used as obtained from the reaction between the amine and N-chlorosuccinimide in ether (ref. 3). <sup>c</sup> Added slowly to the chloroamine; all reactions were exothermic and complete on addition of one equivalent of the olefin. <sup>d</sup> Solvent A, 4 M H<sub>2</sub>SO<sub>4</sub> and 1.5 M H<sub>2</sub>O in acetic acid; solvent B, Eastman White Label trifluoroacetic acid. <sup>e</sup> Up to 10% of the further (ionic) condensation products (R<sub>2</sub>NCH<sub>2</sub>CH=)<sub>2</sub> were also obtained. <sup>f</sup> B.p. 99° (1.5 mm.), *n*<sub>D</sub><sup>20</sup> 1.4600, picrate m.p. 87.5-89.5°, hydrochloride m.p. 95.5-97.5°. <sup>g</sup> In a quartz vessel with irradiation from a Hanovia No 616A medium pressure mercury arc source. <sup>h</sup> B.p. 86° (0.05 mm.), *n*<sub>D</sub><sup>20</sup> 1.4600, [R<sub>2</sub>NCH<sub>2</sub>CH=]<sub>2</sub>-dipicrate m.p. 144-145°. <sup>i</sup> Obtained by LiAlH<sub>4</sub> reduction of the unusually reactive adduct Vc initially isolated; b.p. 62° (0.02 mm.), *n*<sub>D</sub><sup>20</sup> 1.5006. <sup>j</sup> Obtained by acetylation of the trifluoroacetate salt of the corresponding chloro adduct V, cf. text; b.p. 77.5° (1.5 mm.), *n*<sub>D</sub><sup>20</sup> 1.4466. <sup>k</sup> B.p. 92.5-93.5° (2 mm.), *n*<sub>D</sub><sup>20</sup> 1.4908-1.4917. <sup>l</sup> B.p. 86.5-88° (3 mm.), *n*<sub>D</sub><sup>20</sup> 1.4926-1.4940.

avoiding prior isolation of the chloro adduct in a separate, tedious basification step.

In contrast to the free radical addition of Ia to butadiene, only ionic chlorination was observed when this chloroamine was treated under nitrogen with the monoolefin 1,1-diphenylethylene; 1-chloro-2,2-diphenylethylene was isolated in 65% yield (Table I, entry 9). Further evidence of the dual ability, thereby defined, of a chloroamine in strongly acidic media to provide cationic chlorine or to undergo radical addition to a diene was sought when N-chlorodiethylamine was treated with norbornadiene under nitrogen (Table I, entry 10). Approximately equal yields of neutral and of basic products were obtained. The former, isolated by dilution of the reaction mixture with water, consisted mainly (>90%) of 3-acetoxy-5-chloronortricyclene (VI) along with a small amount of the isomeric 2-endo-acetoxy-3-exo-chloro-5-norbornene (VII); the latter, liberated on basification of the diluted solution, consisted of 3-chloro-5-diethylaminonortricyclene (VIII) and the isomeric *exo*-2-diethylamino-*syn*-7-chloro-5-norbornene (IX) in the approximate ratio VIII/IX = 2/3. The structure of compound IX strongly indicates the basic products to have resulted from an ionic reaction involving the skeletal rearrangements presumably observed previously<sup>6</sup> in carbonium ion reactions of norbornadiene. When the reaction was carried out in the presence of air, the products VI-IX were obtained in the same yields as under nitrogen, which strongly supports the supposition of an ionic pathway.

Each of the compounds VI-IX was obtained pure by g.l.c. The proof of structure has been unambiguously carried out for each product, principally by thorough n.m.r. analysis; the details of this reaction and characterization of the products will be described in a forthcoming paper.

(6) S. Winstein and M. Shatavsky, *Chem. Ind.*, (London), 56 (1956).



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### The Preparation of Dihalomethyl Derivatives of Carbon, Silicon, and Germanium by the Action of Phenyl-(trihalomethyl)mercurials on C-H, Si-H, and Ge-H Linkages

Sir:

The high reactivity of phenyl(trihalomethyl)mercurials in reactions with olefins of low reactivity toward dihalocarbenes generated by action of bases on trihalomethide ion sources<sup>1</sup> suggested to us that phenyl(trihalomethyl)mercury compounds might release CX<sub>2</sub> to other types of substrates which are known to react with carbenes. The insertion of methylene itself into C-H bonds is well known.<sup>2</sup> However, only a few isolated cases of dihalocarbene insertion into C-H linkages have been reported,<sup>3,4</sup> and the yields of insertion products were only low to moderate. The insertion of methylene

(1) D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. M. Burlitch, and S. R. Dowd, *J. Org. Chem.*, **28**, 1163 (1963).

(2) E. Chinopoulos, *Chem. Rev.*, **63**, 235 (1963).

(3) E. K. Fields, *J. Am. Chem. Soc.*, **84**, 1744 (1962).

(4) J. C. Anderson and C. B. Reese, *Chem. Ind.* (London), 575 (1963).